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Collection of Emission from an Oscillating Dipole Inside a Sphere: Analytic Integration Over a Circular Aperture

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Abstract

We describe a method for analytically integrating, over a circular aperture, the emission from an oscillating dipole inside a dielectric sphere. The model is useful for investigating fluorescence, Raman, or other emission from molecules inside spherical particles or droplets. The analysis is performed for two cases: (1) the dipole emits from a fixed orientation, and (2) the dipole emits from all orientations. In both cases, all light entering the aperture is collected. The second case models the collection of emission from a molecule that is excited repeatedly; after each excitation, it rotates to a random orientation before emitting. These results are applicable to single-molecule detection techniques employing microdroplets and to other techniques for characterizing microparticles through the use of luminescence or inelastic scattering.

Contents

1. Introduction

Collection of emission from molecules in, on, or near small particles is important for a variety of applications: e.g., detection of single fluorescent molecules in microspheres [1–6], characterization of particles or droplets using fluorescence [7,8] or Raman [9] emission (the particles may be inhomogeneous particles, as in a droplet containing viruses or bacteria), characterization of lasing or nonlinear emission processes [10] or energy transfer [11] in microspheres, determination of the orientation of molecules on the surface of a droplet [12,13], and measurements of cavity quantum electrodynamic effects in spheres [13–16]. Collection of light elastically scattered by inclusions inside droplets [17–19] is a related problem. The irradiance collected by a lens depends on the position of the molecule(s) or scatterer(s) within the particle, because light reflects and refracts at the particle surface.

Fluorescence and Raman emission from molecules inside spheres have been modeled assuming the molecule can be approximated as an oscillating dipole [20–23]. The fields of the dipole and the fields induced inside and outside the sphere are expanded in spherical wave functions, and the expansion coefficients are determined by enforcement of the boundary conditions at the sphere's surface. Real molecules emit with a nonzero transition linewidth. One can approximate the emission over the linewidth by averaging the output over a lineshape function [22].

In earlier work [22,23], Hill et al calculated the collection of fluorescence from a molecule, modeled as an oscillating dipole, using numerical integration over a circular collection aperture. In experimental work, it is often important to maximize the collection solid angle in order to maximize the signal. A problem arises when one uses numerical integration over the aperture: as the solid angle of the collection aperture increases, the number of points needed for accurate numerical integration can become prohibitive; the problem becomes worse as the size of the sphere increases. Problems with integrating over large-solid-angle apertures become even more important in modeling fluorescence or other emission in which the intensity must be integrated over emission frequency [22,23], particularly when high Q morphology-dependent resonances of the spheres are within the emission band.

Methods have been developed for "analytically" integrating, over a circular aperture, the scattering from a sphere illuminated with one or more plane waves [24–30]. In those methods, the integration computations are performed with recursion relations replacing the numerical integration scheme. Since numerical integration is not required, the approach is referred to as "analytical." Advantages of the analytical method are that numerical results do not have to be checked for convergence (as they must be when numerical integration is used), and the analytical method can readily treat solid angles up to 4π sr.

In this report, we show that the emission from a dipole inside a spherical particle can be integrated analytically over a collection aperture. We consider two cases: (1) emission from a dipole with fixed orientation, and (2) emission from a dipole that rotates through all orientations. For case (2), we show how the irradiance collected by the aperture can be obtained by analytical integration over all dipole orientations. The rotating dipole model is appropriate for collection of fluorescent emission from a small molecule (e.g., laser dye) in water, where the molecule is excited repeatedly. In integrating the emitted irradiance over the circular aperture, we apply some of the techniques used previously for scattering by spheres [24–30].

In section 2, we describe the situation to be modeled: the sphere, dipole, electric fields, aperture, and coordinate systems. In section 3, we integrate the irradiance over the circular aperture when the dipole is in a fixed orientation, and provide (in eq (31)) a key result of this report: an explicit expression for the power collected. In section 4, we integrate the collected intensity at the aperture for a rotating dipole, and provide the results in equation (43). We summarize our work in section 5. Four appendices provide mathematical details.

2. The Sphere Dipole Fields and Aperture

In this section we define the problem (sphere, dipole, aperture, fields) for which we derive analytic solutions in sections 3 and 4. The region inside the sphere, region 1 with refractive index N_1, is assumed to be homogeneous, except for one or more oscillating dipoles. The effect of any dipole (molecule) on the absorption of emission from other dipoles is included in the homogeneous refractive index of the sphere. The region outside the sphere, region 2 with refractive index N_2, is infinite and homogeneous, except for the circular aperture and lens, which are far from the sphere. The wavenumbers are $k_0 = \omega/c$ in vacuum, $k_1 = N_1 k_0$ in region 1, and $k_2 = N_2 k_0$ in region 2.

An (x, y, z) Cartesian coordinate system with basis vectors $(\widehat{\mathbf{x}}, \widehat{\mathbf{y}}, \widehat{\mathbf{z}})$ is located with its origin at the center of the sphere. The spherical system associated with the (x, y, z) Cartesian system is the (r, θ, ϕ) system with basis vectors $(\widehat{\mathbf{r}}, \widehat{\boldsymbol{\theta}}, \widehat{\boldsymbol{\phi}})$. The z-axis, by definition, extends through the center of the circular aperture. An oscillating dipole $\mathbf{p}$, with $\exp(-i\omega t)$ time variation, is located at $\mathbf{r}_d$, and the orientation of the x-axis can be defined with respect to $\mathbf{r}_d$. We do this by giving the results in a form that holds for any chosen orientation of the x-axis.

The coordinates of $\mathbf{r}_d$ in the spherical system are (r_d, θ_d, ϕ_d). The half-plane containing the z-axis and $\mathbf{r}_d$ is at an angle of ϕ_d from the x-axis, and the choice of ϕ_d has the effect of locating the x-axis with respect to $\mathbf{r}_d$. We give the results in a general form that holds for any value of ϕ_d.

Typically, an incident electromagnetic wave would be required to excite the dipole [20] (molecule), although there are exceptions: e.g., chemiluminescence and emission of thermal photons. We do not treat the problem of excitation of the dipole here. Methods of calculating the internal fields of spheres illuminated with plane waves [20,31,32], counterpropagating plane waves [23], or Gaussian beams [33,34] are well understood. For a molecule with a rotational diffusion time that is short compared to its average emission time, the excitation and emission problems can be separated (as described elsewhere [23]).

The electric field produced at $\mathbf{r}$ in region 2 by dipole $\mathbf{p}$ at $\mathbf{r}_d$ in region 1 can be expressed as

$$\mathbf{E}(\mathbf{r}) = \omega^2 \mu_2 \, \mathbf{G}(\mathbf{r}, \mathbf{r}_d) \cdot \mathbf{p}(\mathbf{r}_d), \tag{1}$$

where $\mathbf{G}(\mathbf{r}, \mathbf{r}_d)$ is a dyadic Green function [35] for a source inside a sphere,* written here as

$$\begin{aligned}\mathbf{G}(\mathbf{r}, \mathbf{r}_d) &= \frac{ik_2\mu_2}{4\pi\mu_1} \sum_{n=1}^{\infty} \frac{2}{n(n+1)} \sum_{m=-n}^{n} (-1)^m \Big[c_n \overline{\mathbf{M}}_{nm}^{(3)}(k_2\mathbf{r}) \overline{\mathbf{M}}_{n,-m}^{(1)}(k_1\mathbf{r}_d) \\ &\quad + d_n \overline{\mathbf{N}}_{nm}^{(3)}(k_2\mathbf{r}) \overline{\mathbf{N}}_{n,-m}^{(1)}(k_1\mathbf{r}_d) \Big]. \qquad (2)\end{aligned}$$

The c_n and d_n are the internal field coefficients for region 1 as defined by Bohren and Huffman [31]. The $\overline{\mathbf{M}}_{nm}^{(q)}$ and $\overline{\mathbf{N}}_{nm}^{(q)}$ are the complex normalized vector spherical harmonics [36]

$$\overline{\mathbf{M}}_{nm}^{(q)}(k\mathbf{r}) \equiv \nabla \times \left(\mathbf{r} z_n^{(q)}(\rho) \exp(im\phi)\, \overline{P}_{nm}(\cos\theta) \right) \qquad (3a)$$

$$= i z_n^{(q)}(\rho) \exp(im\phi) \left[\hat{\boldsymbol{\theta}}\, \overline{\pi}_{nm}(\cos\theta) + i\hat{\boldsymbol{\phi}} \overline{\tau}_{nm}(\cos\theta) \right], \qquad (3b)$$

$$\overline{\mathbf{N}}_{nm}^{(q)}(k\mathbf{r}) \equiv \frac{1}{k} \nabla \times \overline{\mathbf{M}}_{nm}^{(q)}(k\mathbf{r}) \qquad (4a)$$

$$\begin{aligned}&= \exp(im\phi) \Big[\hat{\mathbf{r}} n(n+1) \frac{z_n^{(q)}(\rho)}{\rho} \overline{P}_{nm}(\cos\theta) \\ &\quad + \frac{(d/d\rho)\left(\rho z_n^{(q)}(\rho)\right)}{\rho} \left(\hat{\boldsymbol{\theta}}\, \overline{\tau}_{nm}(\cos\theta) + i\hat{\boldsymbol{\phi}} \overline{\pi}_{nm}(\cos\theta) \right) \Big], \qquad (4b)\end{aligned}$$

where $\rho \equiv kr$, the $z_n^{(q)}(kr)$ are spherical Bessel functions $j_n(kr)$ when $q = 1$, and are spherical Hankel functions $h_n^{(1)}(kr)$ when $q = 3$, and where

$$\overline{\pi}_{nm}(\cos\theta) = \frac{m\overline{P}_{nm}(\cos\theta)}{\sin\theta}, \qquad (5)$$

$$\overline{\tau}_{nm}(\cos\theta) = (d/d\theta)\overline{P}_{nm}(\cos\theta), \qquad (6)$$

where the $\overline{P}_{nm}(\cos\theta)$ are the normalized associated Legendre functions of Arfken [37] and Belousov [38]. Computation of these functions is discussed in appendix A.

*The Green function shown here can be obtained following the approach of Tai [35]. The notation of equation (1) differs from Tai's notation in that it employs the complex vector spherical harmonics (see app B). Tai does the problem for a dipole outside a sphere. We used his approach to do the problem for a dipole inside a sphere.

The dipole is $\mathbf{p} = p\widehat{\mathbf{p}}$, where p is the dipole magnitude and $\widehat{\mathbf{p}}$ is a unit vector in the direction of the dipole axis. The dipole direction $\widehat{\mathbf{p}}$ is specified by the Euler angles α and β (the ϕ and θ angles describing the dipole direction with respect to the (x, y, z) system), such that

$$\widehat{\mathbf{p}} = \sum_{j=1}^{3} f_j \widehat{\mathbf{e}}_j, \tag{7}$$

where $(\widehat{\mathbf{e}}_1, \widehat{\mathbf{e}}_2, \widehat{\mathbf{e}}_3) = (\widehat{\mathbf{x}}, \widehat{\mathbf{y}}, \widehat{\mathbf{z}})$ and

$$f_1 = \sin\beta\cos\alpha, \tag{8a}$$
$$f_2 = \sin\beta\sin\alpha, \tag{8b}$$
$$f_3 = \cos\beta. \tag{8c}$$

Using equations (1), (2), and (7), we can write the electric field at $\mathbf{r}$ generated by a dipole at $\mathbf{r}_d$ as

$$\mathbf{E}(\mathbf{r}) = E_{ref} \sum_{n=1}^{\infty} \frac{2i}{n(n+1)} \sum_{m=-n}^{n} \sum_{j=1}^{3} f_j \left[c_{n,-m}^{j} \, \overline{\mathbf{M}}_{nm}^{(3)}(k\mathbf{r}) + d_{n,-m}^{j} \, \overline{\mathbf{N}}_{nm}^{(3)}(k\mathbf{r}) \right], \tag{9}$$

where

$$E_{ref} \equiv \left(\frac{p}{4\pi\varepsilon_0}\right) \left(\frac{(\mu_2)^2}{\mu_0\mu_1}\right) k_2 (k_0)^2, \tag{10}$$
$$c_{n,-m}^{j} \equiv (-1)^m c_n \widehat{\mathbf{e}}_j \cdot \overline{\mathbf{M}}_{n,-m}^{(1)}(k_1\mathbf{r}_d), \tag{11}$$
$$d_{n,-m}^{j} \equiv (-1)^m d_n \widehat{\mathbf{e}}_j \cdot \overline{\mathbf{N}}_{n,-m}^{(1)}(k_1\mathbf{r}_d). \tag{12}$$

All the light emitted into the solid angle intercepted by the aperture is assumed to be collected. The aperture extends from $\theta_{\min}$ to $\theta_{\max}$ and is circular ($0 \leq \phi \leq 2\pi$). The solid angle with $\theta \leq \theta_{\min}$ is covered by a concentric aperture stop. With $d\Omega = \sin\theta \, d\theta \, d\phi$, the aperture solid angle is

$$\Delta\Omega = \int_0^{2\pi} \int_{\theta=\theta_{\min}}^{\theta=\theta_{\max}} d\Omega = 2\pi[\cos(\theta_{\min}) - \cos(\theta_{\max})]. \tag{13}$$

3. Collection of Emission from a Fixed-Orientation Dipole

The radiant power collected by the aperture is

$$P = \int_{\Delta\Omega} d\Omega \, r^2 I(\mathbf{r}), \tag{14}$$

where the irradiance of the emitted light at $\mathbf{r}$ is

$$I(\mathbf{r}) = \frac{N_2}{2\mu_2 c} |\mathbf{E}(\mathbf{r})|^2. \tag{15}$$

Here, we use a dimensionless power collected by the aperture, P_D, defined as

$$P_D \equiv \frac{(k_2)^2}{I_{ref}} P, \tag{16}$$

where I_{ref} is the irradiance of a reference electromagnetic wave,

$$I_{ref} = \frac{N_2}{2\mu_2 c} (E_{ref})^2, \tag{17a}$$

$$= \frac{1}{8\pi} \; \frac{1}{4\pi\varepsilon_0} \; \frac{(\mu_2)^3}{\mu_0(\mu_1)^2} \; c p^2 (k_2)^3 (k_0)^3. \tag{17b}$$

In terms of the electric field, the dimensionless power collected is

$$P_D = \int_{\Delta\Omega} d\Omega (k_2)^2 r^2 \frac{|\mathbf{E}(\mathbf{r})|^2}{(E_{ref})^2} \;. \tag{18}$$

The aperture is in the far field of the sphere. As $\rho_2 \equiv k_2 r$ becomes large, $h_n^{(1)}(\rho_2)$ can be replaced by its asymptotic expression, $(-i)^n[\exp(i\rho_2)]/i\rho_2$, and the $\overline{\mathbf{M}}_{nm}^{(3)}(k_2\mathbf{r})$ and $\overline{\mathbf{N}}_{nm}^{(3)}(k_2\mathbf{r})$ from equations (3b) and (4b) can be written

$$\begin{pmatrix} \overline{\mathbf{M}}_{nm}^{(3)}(k_2\mathbf{r}) \\ \overline{\mathbf{N}}_{nm}^{(3)}(k_2\mathbf{r}) \end{pmatrix} = (-i)^n \frac{\exp(i\rho_2)}{\rho_2} \exp(im\phi) \left[\widehat{\theta} \begin{pmatrix} \overline{\pi}_{nm}(\cos\theta) \\ \overline{\tau}_{nm}(\cos\theta) \end{pmatrix} + i\widehat{\phi} \begin{pmatrix} \overline{\tau}_{nm}(\cos\theta) \\ \overline{\pi}_{nm}(\cos\theta) \end{pmatrix} \right]. \tag{19}$$

Because $I(\mathbf{r})$ is inversely proportional to $(\rho_2)^2$ in the far field, P_D is not a function of r, the distance from the sphere's center to a field point $\mathbf{r}$ on the aperture.

Substituting equation (9) for $\mathbf{E}(\mathbf{r})$ into equation (18), simplifying the result with the help of equation (19), and then integrating over ϕ from 0 to 2π, leads to

$$P_D = 8\pi \sum_{n=1}^{\infty} \sum_{n'=1}^{\infty} \sum_{m=-\min(n,n')}^{\min(n,n')} \sum_{j=1}^{3} \sum_{j'=1}^{3} f_j f_{j'} \left[\left(\psi^{dot}_{nn',-m}\right)^{jj'} \bar{\mathbf{I}}^{dot}_{nn'm} + \left(\psi^{cross}_{nn',-m}\right)^{jj'} \bar{\mathbf{I}}^{cross}_{nn'm} \right], \tag{20}$$

where

$$\left(\psi^{dot}_{nn',-m}\right)^{jj'} \equiv \frac{\left(c^{j}_{n,-m}\, c^{j'*}_{n',-m} + d^{j}_{n,-m}\, d^{j'*}_{n',-m}\right)(-i)^n\,(i)^{n'}}{n(n+1)n'(n'+1)}, \tag{21}$$

$$\left(\psi^{cross}_{nn',-m}\right)^{jj'} \equiv \frac{\left(c^{j}_{n,-m}\, d^{j'*}_{n',-m} + d^{j}_{n,-m}\, c^{j'*}_{n',-m}\right)(-i)^n\,(i)^{n'}}{n(n+1)n'(n'+1)}, \tag{22}$$

and

$$\begin{aligned} \bar{\mathbf{I}}^{cross}_{nn'm} &\equiv \int_{\mu_{\max}}^{\mu_{\min}} d\mu \left(\overline{\pi}_{nm}(\mu)\overline{\tau}_{n'm}(\mu) + \overline{\tau}_{nm}(\mu)\overline{\pi}_{n'm}(\mu)\right), \\ &= \left[-m\overline{P}_{nm}(\mu)\overline{P}_{n'm}(\mu)\right]_{\mu_{\max}}^{\mu_{\min}}, \end{aligned} \tag{23}$$

where $\mu \equiv \cos\theta$, $\mu_{\min} \equiv \cos\theta_{\min}$, and $\mu_{\max} \equiv \cos\theta_{\max}$, and

$$\bar{\mathbf{I}}^{dot}_{nn'm} \equiv \int_{\mu_{\max}}^{\mu_{\min}} d\mu \left(\overline{\pi}_{nm}(\mu)\overline{\pi}_{n'm}(\mu) + \overline{\tau}_{nm}(\mu)\overline{\tau}_{n'm}(\mu)\right). \tag{24}$$

The evaluation of $\bar{\mathbf{I}}^{dot}_{nn'm}$ requires consideration of two cases. When $n \neq n'$,

$$\bar{\mathbf{I}}^{dot}_{nn'm} = \left[(-1)\frac{\left[n(n+1)\overline{P}_{nm}(\mu)\sqrt{1-\mu^2}\,\overline{\tau}_{n'm}(\mu) - n'(n'+1)\overline{P}_{n'm}(\mu)\sqrt{1-\mu^2}\,\overline{\tau}_{nm}(\mu)\right]}{n(n+1) - n'(n'+1)}\right]_{\mu_{\max}}^{\mu_{\min}}. \tag{25}$$

When $n = n'$, $\bar{\mathbf{I}}^{dot}_{nnm}$ is obtained with the relation

$$\bar{\mathbf{I}}^{dot}_{nnm} = \left[(-1)\overline{P}_{nm}(\mu)\sqrt{1-\mu^2}\,\overline{\tau}_{nm}(\mu)\right]_{\mu_{\max}}^{\mu_{\min}} + n(n+1)\overline{I}_{nnm}, \tag{26}$$

where

$$\begin{aligned}\overline{I}_{nnm} &\equiv \int_{\mu_{\max}}^{\mu_{\min}} d\mu \left(\overline{P}_{nm}(\mu)\right)^2, \\ &= \left[\frac{\overline{P}_{nm}(\mu)\sqrt{1-\mu^2 P}_{n,m-1}(\mu)}{\sqrt{(n+m)(n-m+1)}}\right]_{\mu_{\max}}^{\mu_{\min}} + \overline{I}_{nn,m-1}. \end{aligned} \tag{27}$$

The evaluation of the above integrals is discussed in appendix C.

The expression for the power collected, equation (20), can be simplified further: First, we use the general result,

$$\sum_{m=-M}^{M} F_m = \sum_{m=0}^{M} \epsilon_m \frac{1}{2}\left(F_m + F_{-m}\right), \tag{28}$$

where ϵ_m is the Neumann function defined as $\epsilon_0 = 1$ and $\epsilon_m = 2$ for $m \neq 0$; second, we use the relations

$$\overline{\mathbf{I}}^{dot}_{nn',-m} = \overline{\mathbf{I}}^{dot}_{nn'm}, \tag{29a}$$

$$\overline{\mathbf{I}}^{cross}_{nn',-m} = -\overline{\mathbf{I}}^{cross}_{nn'm}. \tag{29b}$$

Equations (29) above are obtained with

$$\overline{P}_{n,-m}(\mu) \equiv (-1)^m \overline{P}_{nm}(\mu), \tag{30a}$$

$$\overline{\pi}_{n,-m}(\mu) = (-1)^{m+1} \overline{\pi}_{nm}(\mu), \tag{30b}$$

$$\overline{\tau}_{n,-m}(\mu) = (-1)^m \overline{\tau}_{nm}(\mu), \tag{30c}$$

which follow from the function definitions. Using equations (20) and (28) to (30), we obtain our final result for the normalized power analytically integrated over the aperture:

$$\begin{aligned} P_D = 4\pi \sum_{n=1}^{\infty}\sum_{n'=1}^{\infty}\sum_{m=0}^{\min(n,n')} \epsilon_m &\left[\overline{\mathbf{I}}^{dot}_{nn'm} \sum_{j=1}^{3}\sum_{j'=1}^{3} f_j f_{j'} \left[\left(\psi^{dot}_{nn'm}\right)^{jj'} + \left(\psi^{dot}_{nn',-m}\right)^{jj'}\right]\right. \\ &\left. - \overline{\mathbf{I}}^{cross}_{nn'm} \sum_{j=1}^{3}\sum_{j'=1}^{3} f_j f_{j'} \left[(\psi^{cross}_{nn'm})^{jj'} - \left(\psi^{cross}_{nn',-m}\right)^{jj'}\right]\right]. \end{aligned} \tag{31}$$

The sums over $f_j f_{j'} \left(\psi^{dot}_{nn'm}\right)^{jj'}$ and $f_j f_{j'} \left(\psi^{cross}_{nn'm}\right)^{jj'}$ are

$$\begin{aligned}\sum_{j=1}^{3}\sum_{j'=1}^{3} f_j f_{j'} \left(\psi^{dot}_{nn'm}\right)^{jj'} &= \frac{(-i)^n (i)^{n'}}{n(n+1)n'(n'+1)} \\ &\times\left[\left(\sum_j f_j c^j_{nm}\right)\left(\sum_{j'} f_{j'} c^{j'}_{n'm}\right)^* \right.\\ &\left.+\left(\sum_j f_j d^j_{nm}\right)\left(\sum_{j'} f_{j'} d^{j'}_{n'm}\right)^*\right], \qquad (32)\end{aligned}$$

and

$$\begin{aligned}\sum_{j=1}^{3}\sum_{j'=1}^{3} f_j f_{j'} \left(\psi^{cross}_{nn'm}\right)^{jj'} &= \frac{(-i)^n (i)^{n'}}{n(n+1)n'(n'+1)} \\ &\times\left[\left(\sum_j f_j c^j_{nm}\right)\left(\sum_{j'} f_{j'} d^{j'}_{n'm}\right)^* \right.\\ &\left.+\left(\sum_j f_j d^j_{nm}\right)\left(\sum_{j'} f_{j'} c^{j'}_{n'm}\right)^*\right], \qquad (33)\end{aligned}$$

where the sums can be expanded as

$$\sum_{j=1}^{3} f_j c^j_{nm} = (-1)^m c_n\left[\sum_{j=1}^{3} f_j \hat{\mathbf{e}}_j \cdot \overline{\mathbf{M}}^{(1)}_{nm}\right] \qquad (34a)$$

$$\begin{aligned}&= (-1)^m c_n j_n(\rho_d) i \exp(im\phi_d)\Big[\Big[\sin\beta\cos\theta_d\cos(\alpha-\phi_d) \\ &\quad -\cos\beta\sin\theta_d\Big]\bar{\pi}_{nm}(\cos\theta_d) \\ &\quad +\sin\beta\sin(\alpha-\phi_d) i\bar{\tau}_{nm}(\cos\theta_d)\Big], \qquad (34b)\end{aligned}$$

and

$$\sum_{j=1}^{3} f_j d_{nm}^{j} = (-1)^m d_n \left[\sum_{j=1}^{3} f_j \hat{\mathbf{e}}_j \cdot \overline{\mathbf{N}}_{nm}^{(1)}\right] \tag{35a}$$

$$\begin{aligned} &= (-1)^m d_n \exp(im\phi_d)\Bigg[\Big[\sin\beta\cos\theta_d\cos(\alpha-\phi_d) - \cos\beta\sin\theta_d\Big] \\ &\times n(n+1)\frac{j_n(\rho_d)}{\rho_d}P_{nm}(\cos\theta_d) + \Bigg(\Big[\sin\beta\cos\theta_d\cos(\alpha-\phi_d) \\ &- \cos\beta\sin\theta_d\Big]\bar{\tau}_{nm}(\cos\theta_d)\Bigg) \\ &+ \sin\beta\sin(\alpha-\phi_d) i\bar{\pi}_{nm}(\cos\theta_d) \times \left(\frac{1}{\rho_d}\frac{d(\rho_d j_n(\rho_d))}{d\rho_d}\right)\Bigg]. \end{aligned} \tag{35b}$$

To evaluate the terms with $-m$, i.e., $\left(\psi_{nn',-m}^{dot}\right)^{jj'}$ and $\left(\psi_{nn',-m}^{cross}\right)^{jj'}$ in equation (31), we rewrite equations (32) to (35) with $m \to (-m)$. Then equations (30) are used to evaluate the rewritten versions of equations (34) and (35).

4. Collection of Emission from a Rotating Dipole

A fluorescent molecule in a low-viscosity liquid may, after absorbing a photon, rotate many times before emitting a photon. For example, the rotational diffusion time for R6G in water is a few picoseconds, while the average time before emission is ∼3 ns. In cases where the collection time is much longer than 3 ns, many photons are emitted in all directions from a rapidly rotating molecule as the fluorescence is collected, and we can obtain the resulting signal by averaging over all orientations of the rotating molecule.

Any function $g(\alpha, \beta)$, where α and β are the Euler angles, can be averaged over orientations with the expression

$$\{g(\alpha,\beta)\} \equiv \frac{1}{4\pi}\int_{\alpha=0}^{2\pi} d\alpha \int_{\beta=0}^{2\pi} d\beta \sin\beta \; g(\alpha,\beta). \tag{36}$$

We substitute $f_j f_{j'}$ for $g(\alpha, \beta)$ in this equation, use the definitions of equations (8), and evaluate the integrals to give

$$\{f_j f_{j'}\} = \frac{1}{3}\delta_{jj'}, \tag{37}$$

where $\delta_{jj'}$ is the Kronecker delta function.

We obtain the portion of the dimensionless power (emitted by a randomly rotating dipole) that is collected by the aperture $\{P_D\}$, by averaging P_D (given in eq (31)) over all dipole orientations. By using equations (36) and (37), we find the result to be

$$\begin{aligned} \{P_D\} \;=\; & \frac{4\pi}{3}\sum_{n=1}^{\infty}\sum_{n'=1}^{\infty}\sum_{m=0}^{\min(n,n')} \epsilon_m \Bigg[\bar{\mathbf{I}}^{dot}_{nn'm}\sum_{j=1}^{3}\left[\left(\psi^{dot}_{nn'm}\right)^{jj} + \left(\psi^{dot}_{nn',-m}\right)^{jj}\right] \\ & - \bar{\mathbf{I}}^{cross}_{nn'm}\sum_{j=1}^{3}\left[\left(\psi^{cross}_{nn'm}\right)^{jj} - \left(\psi^{cross}_{nn',-m}\right)^{jj}\right]\Bigg]. \end{aligned} \tag{38}$$

Evaluating the sums over j gives

$$\sum_{j=1}^{3}\left(\psi^{dot}_{nn'm}\right)^{jj} = \sum_{j=1}^{3}\left(\psi^{dot}_{nn',-m}\right)^{jj} = \Psi^{dot}_{nn'm}, \tag{39}$$

and

$$\sum_{j=1}^{3} (\psi_{nn'm}^{cross})^{jj} = -\sum_{j=1}^{3} \left(\psi_{nn',-m}^{cross}\right)^{jj} = \Psi_{nn'm}^{cross} + \Psi_{n'nm}^{cross*}, \tag{40}$$

where

$$\begin{aligned}
\Psi_{nn'm}^{dot} \equiv & \left(c_n c_{n'}^* \, \overline{\mathbf{M}}_{nm}^{(1)}(k\mathbf{r}_d) \cdot \overline{\mathbf{M}}_{n'm}^{(1)*}(k\mathbf{r}_d) + d_n d_{n'}^* \, \overline{\mathbf{N}}_{nm}^{(1)}(k\mathbf{r}_d) \cdot \overline{\mathbf{N}}_{n'm}^{(1)*}(k\mathbf{r}_d)\right) \\
& \times \frac{(-i)^n \ (i)^{n'}}{n(n+1)n'(n'+1)}, && (41) \\
\Psi_{nn'm}^{cross} \equiv & \left(c_n d_{n'}^* \, \overline{\mathbf{M}}_{nm}^{(1)}(k\mathbf{r}_d) \cdot \overline{\mathbf{N}}_{n'm}^{(1)*}(k\mathbf{r}_d)\right) \frac{(-i)^n (i)^{n'}}{n(n+1)n'(n'+1)}. && (42)
\end{aligned}$$

The symmetry operation of interchanging the summation indices n and n' in $\Psi_{n'n,m}^{cross*}$ then allows equation (38) to be rewritten as

$$\{P_D\} = \frac{8\pi}{3} \sum_{n=1}^{\infty} \sum_{n'=1}^{\infty} \sum_{m=0}^{\min(n,n')} \epsilon_m \left[\Psi_{nn'm}^{dot} \, \overline{\mathbf{I}}_{nn'm}^{dot} - [2\,\mathrm{Re}\,(\Psi_{nn'm}^{cross})] \, \overline{\mathbf{I}}_{nn'm}^{cross}\right]. \tag{43}$$

The radiant power of the collected emission from a sphere containing a rotating dipole is then computed with the relation

$$\{P\} = \frac{I_{ref}}{(k_2)^2} \, \{P_D\}. \tag{44}$$

In previous work [22,23], it was convenient to use the normalized fluorescence collected $F(\mathbf{r}_d, \omega)$, which is the fluorescence collected from a dipole in a sphere normalized by the fluorescence collected from a dipole in a homogeneous medium, i.e.,

$$F(\mathbf{r}_d, \omega) \equiv \frac{\{P\}}{\{P\}_{\text{hom}}}. \tag{45}$$

To calculate $\{P\}_{\text{hom}}$, we set the medium of the sphere identical to that of the surrounding medium (i.e., $N_1 = N_2$ and $\mu_1 = \mu_2$). We show in appendix D that $\{P_D\}_{\text{hom}} = (2/3)\Delta\Omega$, so that

$$\{P\}_{\text{hom}} = \left(\frac{I_{ref}}{(k_2)^2}\right) \left(\frac{2\Delta\Omega}{3}\right) \tag{46}$$

for any $\Delta\Omega$ and for any position of the dipole within the sphere. The normalized power collected by the aperture is then

$$F(\mathbf{r}_d, \omega) = \frac{4\pi}{\Delta\Omega} \sum_{n=1}^{\infty} \sum_{n'=1}^{\infty} \sum_{m=0}^{\min(n,n')} \epsilon_m \left[\Psi_{nn'm}^{dot} \, \bar{\mathbf{I}}_{nn'm}^{dot} - \left[2 \, \mathrm{Re} \left(\Psi_{nn'm}^{cross} \right) \right] \bar{\mathbf{I}}_{nn'm}^{cross} \right] . \tag{47}$$

5. Summary

We have developed analytical expressions for the power entering a collecting aperture after emission from a dipole inside a spherical particle or droplet. The key results of this report are equations (31) and (43): equation (31) gives the power collected by an aperture when the dipole is in a fixed orientation, and equation (43) gives the power collected by the aperture when the emission is integrated over all dipole orientations.

The results should be useful in modeling experiments in which fluorescence or other emission from molecules inside, on, or near the surface of a sphere is measured. The results for integrating over dipole orientation are useful for modeling a dipole (at a fixed position) when the rotational diffusion time is much smaller than the fluorescence lifetime of the molecule, which in turn is much smaller than the collection time for the experiment; in such an experiment, the molecule absorbs and emits many photons from many different random orientations. An advantage of performing the integrations over the aperture analytically is that one need not test the results for convergence when the size, refractive index, or numerical aperture increase. We suggest that the results presented here may be particularly useful for cases in which the results must be integrated over a large wavelength range and the sphere is in a size range where narrow morphology-dependent resonances strongly influence the emission.

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Appendix A. Computation of the $\overline{P}_{nm}$, $\overline{\pi}_{nm}$, and $\overline{\tau}_{nm}$ Functions

The $\overline{\pi}_{nm}(\mu)$ and $\overline{\tau}_{nm}(\mu)$ functions are defined here as

$$\overline{\pi}_{nm}(\mu) \equiv \frac{m\overline{P}_{nm}(\mu)}{\sqrt{1-\mu^2}}, \tag{A-1}$$

$$\overline{\tau}_{nm}(\mu) \equiv -\sqrt{1-\mu^2}(d/d\mu)\overline{P}_{nm}(\mu), \tag{A-2}$$

where $\overline{P}_{nm}(\mu)$ is the normalized associated Legendre function defined by Arfken [37] and Belousov [38] as

$$\overline{P}_{nm}(\mu) \equiv A_{nm}P_{nm}(\mu), \tag{A-3}$$

where

$$A_{nm} \equiv \sqrt{\frac{(2n+1)(n-m)!}{2(n+m)!}}, \tag{A-4}$$

and

$$P_{nm}(\mu) = (1-\mu^2)^{m/2}\frac{d^m}{d\mu^m}P_n(\mu) \tag{A-5}$$

is the associated Legendre function as defined by Arfken [37] and Stratton [39] and used in the standard light scattering references by Bohren and Huffman [31] and van de Hulst [40]. These Legendre functions differ by a factor of $(-1)^m$ from the Legendre functions used by Jackson [41], Abramowitz and Stegun [42], and Gradshteyn and Ryzhik [43]. These last two references are of particular interest for their extensive recursion relations, but care must be exercised because of the $(-1)^m$ factor difference. The $\overline{\pi}_{nm}$ and $\overline{\tau}_{nm}$ functions are defined here to agree with Fuller's definitions [44], except with an additional factor of A_{nm}. There is a computational advantage to using normalized Legendre functions, because the factorials in A_{nm} do not have to be computed separately but are incorporated into the recursion relations.

We can obtain two relations convenient for computing $\overline{P}_{nm}(\mu)$, $\overline{\pi}_{nm}(\mu)$, and $\overline{\tau}_{nm}(\mu)$ by rewriting equations (8.733) given by Gradshteyn and Ryzhik [43] as

$$\begin{aligned} \mu\overline{\pi}_{nm}(\mu) &= \left(\frac{1}{2}\right)\Big[\sqrt{(n-m+1)(n+m)}\overline{P}_{n,m-1}(\mu) \\ &\quad + \sqrt{(n+m+1)(n-m)}\overline{P}_{n,m+1}(\mu)\Big], \qquad \text{(A-6)} \\ \overline{\tau}_{nm}(\mu) &= \left(\frac{1}{2}\right)\Big[\sqrt{(n-m+1)(n+m)}\overline{P}_{n,m-1}(\mu) \\ &\quad - \sqrt{(n+m+1)(n-m)}\overline{P}_{n,m+1}(\mu)\Big]. \qquad \text{(A-7)} \end{aligned}$$

If $\mu \neq 1$, then equation (A-1) is used to compute $\overline{\pi}_{nm}(\mu)$ from $\overline{P}_{nm}(\mu)$, and the above two relations are used to compute $\overline{P}_{n,m+1}(\mu)$ and $\overline{\tau}_{nm}(\mu)$.

If $\mu = 1$, then

$$\overline{P}_{nm}(1) = \sqrt{\frac{(2n+1)}{2}}\delta_{m,0}, \qquad \text{(A-8)}$$

and equations (A-6) and (A-7) become

$$\overline{\pi}_{nm}(1) = \frac{1}{2}\sqrt{\frac{(2n+1)n(n+1)}{2}}\left(\delta_{m,1} + \delta_{m,-1}\right), \qquad \text{(A-9)}$$

$$\overline{\tau}_{nm}(1) = \frac{1}{2}\sqrt{\frac{(2n+1)n(n+1)}{2}}\left(\delta_{m,1} - \delta_{m,-1}\right). \qquad \text{(A-10)}$$

Appendix B. The Green Function

Using the traditional vector spherical harmonics, Tai [35] writes the equations necessary to solve for the Green functions when the dipole is outside the sphere. Tai [35] does not explicitly give the results for his coefficients A_n, B_n, C_n, and D_n. However, when his equations are solved, his upper case coefficients can be seen to be related to the lower case sphere coefficients of Bohren and Huffman [31], as

$$\begin{aligned} A_n &= -b_n, \\ B_n &= -a_n, \\ C_n &= c_n, \\ D_n &= d_n. \end{aligned} \tag{B-1}$$

The Green functions for a dipole inside the sphere can be obtained with essentially the same approach used by Tai [35] for the external dipole, and we obtain the result for the region outside the sphere as

$$\begin{aligned} \mathbf{G}(\mathbf{r}, \mathbf{r}_d) \;=\; & \frac{ik_2\mu_2}{4\pi\mu_1} \sum_{n=1}^{\infty} \frac{2}{n(n+1)} \sum_{m=0}^{n} \epsilon_m (A_{nm})^2 \sum_{\sigma=e,o} \Big[c_n\, \mathbf{M}^{(3)}_{\sigma mn}(k_2\mathbf{r})\, \mathbf{M}^{(1)}_{\sigma mn}(k_1\mathbf{r}_d) \\ & + d_n \mathbf{N}^{(3)}_{\sigma mn}(k_2\mathbf{r})\, \mathbf{N}^{(1)}_{\sigma mn}(k_1\mathbf{r}_d) \Big] . \end{aligned} \tag{B-2}$$

To rewrite this result with our vector spherical harmonics (eq (3b) and (4b)), we note that they are related to the traditional ones [31,32,39] by the relations

$$A_{nm}\mathbf{M}^{(q)}_{emn} \;=\; \frac{1}{2}\left(\overline{\mathbf{M}}^{(q)}_{nm} + (-1)^m \overline{\mathbf{M}}^{(q)}_{n,-m}\right), \tag{B-3}$$

$$A_{nm}\mathbf{M}^{(q)}_{omn} \;=\; \frac{1}{2i}\left(\overline{\mathbf{M}}^{(q)}_{nm} - (-1)^m \overline{\mathbf{M}}^{(q)}_{n,-m}\right), \tag{B-4}$$

$$A^{(q)}_{nm}\mathbf{N}_{emn} \;=\; \frac{1}{2}\left(\overline{\mathbf{N}}^{(q)}_{nm} + (-1)^m \overline{\mathbf{N}}^{(q)}_{n,-m}\right), \tag{B-5}$$

$$A_{nm}\mathbf{N}^{(q)}_{omn} \;=\; \frac{1}{2i}\left(\overline{\mathbf{N}}^{(q)}_{nm} - (-1)^m \overline{\mathbf{N}}^{(q)}_{n,-m}\right), \tag{B-6}$$

where A_{nm} is defined in equation (A-4).

Using equations (B-3) to (B-6) we rewrite the Green function as

$$\begin{aligned}
\mathbf{G}(\mathbf{r},\mathbf{r}_d) \;=\; & \frac{ik_2\mu_2}{4\pi\mu_1}\sum_{n=1}^{\infty}\frac{1}{n(n+1)}\sum_{m=0}^{n}\epsilon_m(-1)^m \\
& \times\Big[c_n\Big(\overline{\mathbf{M}}^{(3)}_{nm}(k_2\mathbf{r})\,\overline{\mathbf{M}}^{(1)}_{n,-m}(k_1\mathbf{r}_d)+\overline{\mathbf{M}}^{(3)}_{n,-m}(k_2\mathbf{r})\,\overline{\mathbf{M}}^{(1)}_{nm}(k_1\mathbf{r}_d)\Big) \\
& + d_n\Big(\overline{\mathbf{N}}^{(3)}_{nm}(k_2\mathbf{r})\,\overline{\mathbf{N}}^{(1)}_{n,-m}(k_1\mathbf{r}_d)+\overline{\mathbf{N}}^{(3)}_{n,-m}(k_2\mathbf{r})\,\overline{\mathbf{N}}^{(1)}_{nm}(k_1\mathbf{r}_d)\Big)\Big].
\end{aligned} \tag{B-7}$$

Then using the general relation for sums given in equation (28), we obtain

$$\begin{aligned}
\mathbf{G}(\mathbf{r},\mathbf{r}_d) \;=\; & \frac{ik_2\mu_2}{4\pi\mu_1}\sum_{n=1}^{\infty}\frac{2}{n(n+1)}\sum_{m=-n}^{n}(-1)^m \\
& \times\left[c_n\,\overline{\mathbf{M}}^{(3)}_{nm}(k_2\mathbf{r})\,\overline{\mathbf{M}}^{(1)}_{n,-m}(k_1\mathbf{r}_d)+d_n\overline{\mathbf{N}}^{(3)}_{nm}(k_2\mathbf{r})\,\overline{\mathbf{N}}^{(1)}_{n,-m}(k_1\mathbf{r}_d)\right].
\end{aligned} \tag{B-8}$$

Appendix C. Evaluation of I^{dot} and I^{cross}

The result for $\bar{\mathbf{I}}^{cross}_{nn'm}$ given in equation (23) in the body of the report is obtained by inspection.

We can prove the expressions for $\bar{\mathbf{I}}^{dot}_{nn'm}$ (eq (25) to (27)) by taking the derivative with respect to μ of both sides of the equations, and then using equations (A-1) and (A-2). Equation (27) can be proved with the help of

$$\overline{P}_{n,m-1}(\mu) = \frac{\mu\overline{\pi}_{nm}(\mu) + \overline{\tau}_{nm}(\mu)}{\sqrt{(n+m)(n-m+1)}}, \tag{C-1}$$

which we obtain by adding equations (A-6) and (A-7). It is also helpful to know that the differential equation for the associated Legendre function can be written as

$$\frac{d}{d\mu}\left(\sqrt{1-\mu^2}\,\overline{\tau}_{nm}(\mu)\right) = n(n+1)\overline{P}_{nm}(\mu) - \frac{m\overline{\pi}_{nm}(\mu)}{\sqrt{1-\mu^2}}. \tag{C-2}$$

Appendix D. $\{P_D\}$ in a Homogeneous Medium

To check the derivations and to obtain a value for normalization, we set the medium of the sphere identical to the medium surrounding the sphere (i.e., $N_1 = N_2$ and $\mu_1 = \mu_2$, where both N_1 and N_2 are real). Then equation (43) can be shown to give the result $\{P_D\} = (2/3)\Delta\Omega$ for any $\Delta\Omega$ and for any position of the dipole within the sphere. We start with a proof for $\Delta\Omega = 4\pi$, and extend that result with an intuitive argument to arbitrary $\Delta\Omega$.

If $N_1 = N_2$ and $\mu_1 = \mu_2$, then $c_n = d_n = 1$. Further, if $\Delta\Omega = 4\pi$, then $\overline{\mathbf{I}}^{dot}_{nn'm} = n(n+1)\delta_{nn'}$ and $\overline{\mathbf{I}}^{cross}_{nn'm} = 0$, so that equation (43) becomes

$$\{P_D\}^{\Delta\Omega=4\pi}_{\text{hom}} = \frac{8\pi}{3}\sum_{n=1}^{\infty}\sum_{m=0}^{n}\frac{\epsilon_m\Big(|\overline{\mathbf{M}}^{(1)}_{nm}(k_1\mathbf{r}_d)|^2 + |\overline{\mathbf{N}}^{(1)}_{nm}(k_1\mathbf{r}_d)|^2\Big)}{n(n+1)}. \qquad \text{(D-1)}$$

Because N_1 is real here, $\rho_d \equiv k_1 r_d$ is also real. This allows the $|\overline{\mathbf{M}}^{(1)}_{nm}(k_1\mathbf{r}_d)|^2$ and $|\overline{\mathbf{N}}^{(1)}_{nm}(k_1\mathbf{r}_d)|^2$ to be written as

$$|\overline{\mathbf{M}}^{(1)}_{nm}(k_1\mathbf{r}_d)|^2 = (j_n(\rho_d))^2\left([\overline{\pi}_{nm}(\cos\theta_d)]^2 + [\overline{\tau}_{nm}(\cos\theta_d)]^2\right), \qquad \text{(D-2)}$$

$$\begin{aligned}|\overline{\mathbf{N}}^{(1)}_{nm}(k_1\mathbf{r}_d)|^2 &= n^2(n+1)^2\left(\frac{j_n(\rho_d)}{\rho_d}\right)^2\left(\overline{P}_{nm}(\cos\theta_d)\right)^2 \\ &\quad + \left(\frac{(d/d\rho_d)\,(\rho_d\, j_n(\rho_d))}{\rho_d}\right)^2\left([\overline{\pi}_{nm}(\cos\theta_d)]^2 + [\overline{\tau}_{nm}(\cos\theta_d)]^2\right). \qquad \text{(D-3)}\end{aligned}$$

The addition theorem for spherical harmonics given by Arfken (eq (12.197), p 694) [37] can be rewritten as

$$\sum_{m=0}^{n}\epsilon_m\left(\overline{P}_{nm}(\cos\theta_d)\right)^2 = \frac{2n+1}{2}, \qquad \text{(D-4)}$$

and a summation over vector-spherical harmonics given by Jackson (eq (16.77), p 753) [41] can be rewritten as

$$\sum_{m=0}^{n}\epsilon_m\Big[\left(\overline{\pi}_{nm}(\cos\theta_d)\right)^2 + \left(\overline{\tau}_{nm}(\cos\theta_d)\right)^2\Big] = \frac{(2n+1)n(n+1)}{2}, \qquad \text{(D-5)}$$

so that

$$\{P_D\}_{\text{hom}}^{\Delta\Omega=4\pi} = \frac{4\pi}{3}\sum_{n=1}^{\infty}(2n+1)\Bigg[\Big(j_n(\rho_d)\Big)^2 + n(n+1)\left(\frac{j_n(\rho_d)}{\rho_d}\right)^2 + \left(\frac{(d/d\rho_d)(\rho_d j_n(\rho_d))}{\rho_d}\right)^2\Bigg]. \tag{D-6}$$

The Rayleigh equation (Arfken [37], p 665) gives

$$\exp(i\rho_d\mu) = \sum_{n=0}^{\infty} i^n(2n+1)j_n(\rho_d)P_n(\mu), \tag{D-7}$$

where $P_n(\mu)$ is a Legendre polynomial. Multiplying each side of equation (D-7) by its complex conjugate and integrating over μ from -1 to 1 gives

$$\sum_{n=1}^{\infty}(2n+1)\left(j_n(\rho_d)\right)^2 = 1 - \left(j_0(\rho_d)\right)^2. \tag{D-8}$$

The Rayleigh equation can be used in essentially the same way to obtain the result

$$\sum_{n=1}^{\infty}(2n+1)\left(\frac{(d/d\rho_d)\,(\rho_d j_n(\rho_d))}{\rho_d}\right)^2 = \frac{1}{3} + \frac{1}{(\rho_d)^2} - \left(\frac{(d/d\rho_d)\,(\rho_d\, j_0(\rho_d))}{\rho_d}\right)^2. \tag{D-9}$$

By using the differential equation of the Legendre polynomial and the Rayleigh equation (D-7), and then multiplying and integrating as before, one can obtain the result

$$\sum_{n=1}^{\infty}(2n+1)n(n+1)\left(\frac{j_n(\rho_d)}{\rho_d}\right)^2 = \frac{2}{3}. \tag{D-10}$$

Recalling that $j_0(\rho_d) = [\sin(\rho_d)]/\rho_d$ then allows these three sums to be combined to give the exact result

$$\{P_D\}_{\text{hom}}^{\Delta\Omega=4\pi} = \frac{8\pi}{3}. \tag{D-11}$$

Because the emission from a randomly rotating dipole in a homogeneous medium is isotropic in the far field, the power $\{P_D\}$ collected by an aperture solid angle $\Delta\Omega$ in the far field is simply proportional to $\Delta\Omega$. Then

$$\begin{aligned}\{P_D\}_{\text{hom}} &= \left(\frac{8\pi}{3}\right)\left(\frac{\Delta\Omega}{4\pi}\right)\\ &= \frac{2}{3}\Delta\Omega\end{aligned} \tag{D-12}$$

is an exact result for all $\Delta\Omega$.

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We describe a method for analytically integrating, over a circular aperture, the emission from an oscillating dipole inside a dielectric sphere. The model is useful for investigating fluorescence, Raman, or other emission from molecules inside spherical particles or droplets. The analysis is performed for two cases: (1) the dipole emits from a fixed orientation, and (2) the dipole emits from all orientations. In both cases, all light entering the aperture is collected. The second case models the collection of emission from a molecule that is excited repeatedly; after each excitation, it rotates to a random orientation before emitting. These results are applicable to single-molecule detection techniques employing microdroplets and to other techniques for characterizing microparticles through the use of luminescence or inelastic scattering.

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